

CPP 39: Focus Session: Ultrafast Processes in Organic Semiconductors and Perovskites I (joint session O/CPP)

The fundamental processes determining the fate of excitons or charge carriers in organic semiconductors or perovskites are happening on an ultrafast timescale, i.e. 100 fs to 10 ps. This, for example, includes singlet-fission, excimer and polaron formation or hot carrier relaxation. Thus, for the development of efficient opto-electronic devices a deep understanding of the processes on this time scale is of utmost importance. Most importantly, theoretical and experimental methods must be combined to successfully decipher the studied phenomena as the many degrees of freedom in these soft matter materials often defy a straightforward explanation from the data. This Focus Session brings together theoretical and experimental scientists fostering an exchange of ideas on the various computational and experimental methods of the ultrafast sciences to the field of organic semiconductors and perovskites.

Organizers: Sebastian Hammer (U Montreal), Petra Tegeder (U Heidelberg)

Time: Thursday 10:30–13:00

Location: MA 004

Topical Talk

CPP 39.1 Thu 10:30 MA 004

Transport and trapping in molecular materials at the picosecond time scale — ●MARINA GERHARD — Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Germany

The Excitonic character of photoexcited states and the soft lattice of organic semiconductors pose guidelines for the design of devices, which are substantially different from those of their inorganic counterparts. To exploit the benefits of organic semiconductors, it is essential to comprehend the fate of photogenerated excitons at early times after their generation. In this context, molecular materials with a well-defined structure serve as ideal model systems to study processes such as exciton transport, excimer formation, singlet fission and energetic funneling. This contribution focuses on two recent studies, in which we explore the exciton dynamics in molecular systems using time and spatially resolved photoluminescence spectroscopy. For tetracene, the transport of excitons is driven by the interplay between singlet fission and triplet fusion. We demonstrate that this peculiar transport mechanism shows a pronounced temperature dependence and that it is severely hampered by the presence of trap states. The second study investigates heterostructures comprised of anthradithiophene with small concentrations of pentacene, which can efficiently mediate singlet fission through a favorable energy level arrangement of both compounds, demonstrating a system in which exciton funneling opens the possibility to spatially and spectrally separate light harvesting and singlet fission moieties.

CPP 39.2 Thu 11:00 MA 004

Fluctuations and exciton dynamics in molecular semiconductors — ●ALEXANDER NEEF¹, SAMUEL BEAULIEU², SEBASTIAN HAMMER³, SHUO DONG⁴, TOMMASO PINCELLI^{1,5}, JULIAN MAKLAR¹, R.PATRICK XIAN⁶, ANKE KRUEGER⁷, MARTIN WOLF¹, LAURENZ RETTIG¹, JENS PFLAUM⁸ and RALPH ERNSTORFER^{1,5} — ¹Fritz-Haber-Institut — ²Centre Lasers Intenses et Applications (CELIA) — ³McGill University — ⁴Chinese Academy of Sciences — ⁵Technical University Berlin — ⁶University of Toronto — ⁷University of Stuttgart — ⁸University of Wuerzburg

Time- and angle-resolved photoemission spectroscopy (trARPES) is a cutting-edge technique to study the electronic structure of materials out-of-equilibrium. Advances in instrumentation now allow taking multidimensional photoemission data sets of delocalized electrons in conventional semiconductors and the reconstruction of spatially confined molecular orbitals. I will present our recent results on trARPES studies of the fluctuation-dominated electronic structure of molecular semiconductors. Furthermore, I will talk about how trARPES made it possible to decipher a complex multiexcitonic process: singlet exciton fission [1]. Apart from the answers gained, a pressing question emerged: how can singlet exciton fission go uphill in energy in certain systems? Our work highlights the need for theories that are able to capture the behavior of excited states in a fluctuating landscape.

[1] Neef et al., Nature 616 (2023) <https://www.nature.com/articles/s41586-023-05814-1>

CPP 39.3 Thu 11:15 MA 004

Efficient Intramolecular Singlet Fission in Weakly-Interacting Heterodimers — ●OSKAR KEFER¹, LUKAS AHRENS², JIE HAN³, JAN FREUDENBERG², FRANK ROMINGER², ANDREAS DREUW³, UWE H. F. BUNZ², and TIAGO BUCKUP¹ — ¹PCI, Universität Heidelberg, Heidel-

berg — ²OCI, Universität Heidelberg, Heidelberg — ³IWR, Universität Heidelberg, Heidelberg

Intramolecular singlet fission (iSF) converts one excited singlet (S_1S_0) into two triplets when two chromophores are covalently bound by a bridge. The bridge also determines the strength of intramolecular interaction. Usually, strong interaction leads to fast formation of the intermediate correlated triplet-pair ($^1[T_1T_1]$), but also hinders its dissociation. A Spiro-linker enforces a perpendicular π -system-arrangement around the central spiro-carbon, leading to long triplet-lifetimes that favor separation into $T_1 + T_1$ without compromising $^1[T_1T_1]$ -formation efficiency.

We expand on this approach and demonstrate a new class of heterodimers that exploit the favorable properties of spiro-conjugation with enhanced iSF dynamics. Quantum-chemical calculations (DFT) and transient absorption spectroscopy link accelerated iSF-kinetics to changes in the S_1S_0 - and $^1[T_1T_1]$ -energy landscape. The limited interaction during the lifetime of $^1[T_1T_1]$ creates favorable conditions for triplet-separation, which are formed with a yield of up to 174%. This new approach furnishes efficient heterogeneous iSF materials with reduced intramolecular interaction due to spatial fixation between chromophores and large, tunable absorption bandwidths.

Topical Talk

CPP 39.4 Thu 11:30 MA 004

Ultrafast charge-transfer dynamics in organic and hybrid interfaces from first principles — ●CATERINA COCCHI — Institut für Physik und CeNaD, Carl von Ossietzky Universität Oldenburg

Charge-transfer dynamics at interfaces in the sub-ps timescale is ruled by complex interplays of electronic and vibrational degrees of freedom. First-principle methods based on real-time time-dependent density functional theory in conjunction with Ehrenfest dynamics offer a practical tool to access and rationalize these phenomena in realistic systems. Considering different organic and hybrid interfaces [1-3], I will discuss the mechanisms ruling charge-transfer dynamics triggered by a resonant pulse. I will illustrate how the intrinsic characteristics of the involved compounds and their mutual interactions affect qualitatively and quantitatively the dynamics of charge carriers in the earliest stages of light-driven coherent excitations. I will highlight methodological aspects that are necessary to reproduce the physics involved [4-6] and point out open issues to be addressed by future developments.

[1] M. Jacobs et al., Adv. Phys. X 5, 1749883 (2020). [2] M. Jacobs et al., ACS Appl. Nano Mater. 5, 5187 (2022). [3] M. Jacobs et al., J. Phys. Chem. A 127, 8794 (2023). [4] J. Krumland et al., J. Chem. Phys. 153, 054106 (2020). [5] J. Krumland et al., Phys. Rev. B 106, 144304 (2022). [6] M. Jacobs et al., arXiv:2311.01776

CPP 39.5 Thu 12:00 MA 004

Charge separation in a porphyrin-based metal organic framework incorporating C₆₀ fullerenes — ●MARTIN RICHTER¹, XIAOJING LIU², PAVEL KOLESNICHENKO¹, CHRISTOF WÖLL², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253/229, 69120 Heidelberg, Germany — ²Institut für Funktionelle Grenzflächen, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Porphyrin-based materials are attracting great interest due to their wide range of applications. They are often embedded into metal organic frameworks (MOF) to manipulate and investigate the relations

between function and structure. Together with an electron acceptor charge separation can be achieved being beneficial for uses e.g. in solar cells or photocatalysis. Experiments on ZnTPP (Zinc 5,15-bis-(3,4,5-trimethoxyphenyl)-10,20-bis-(4-carboxyphenyl)) in a surface anchored MOF (SURMOF) loaded with fullerene C₆₀ inside the pores have shown that photoexcitation increases the conductivity by up to two orders of magnitude.[1] Here, we investigate excited states dynamics after optical excitation with transient absorption spectroscopy on the femto- to nanosecond scale. Charge separated states can be identified, which have a lifetime of a few hundred picoseconds. The charge separation occurs after excitation of both the Soret band and the Q band.

1. X. Liu, *Angew. Chem. Int. Ed.* 2019, 58, 9590.

CPP 39.6 Thu 12:15 MA 004

Ultrafast charge separation and band structure dynamics in metal-phthalocyanine/WSe₂ heterostructures — ●GREGOR ZINKE, SEBASTIAN HEDWIG, BENITO ARNOLDI, MARTIN ANSTETT, MARTIN AESCHLIMANN, and BENJAMIN STADTMÜLLER — University of Kaiserslautern-Landau, Germany

2D-Van-der-Waals materials and their heterostructures are a highly promising class of materials due to their low dimensional nature and diverse electronic properties, especially regarding their charge and spin carrier dynamics. In addition to chemical tunability, the spin-dependent electronic properties of such 2D heterostructures can also be altered on ultrafast timescales by the formation of transient charge-separated states. In this contribution, we focus on optically induced interlayer charge and spin transfer processes in heterostructures consisting of molecule films on the surface of a bulk WSe₂ crystal. Using spin-, time- and angle-resolved photoemission with XUV radiation, we can simultaneously monitor the excited carriers as well as the corresponding hole dynamics. For molecule films made of the metal phthalocyanines (MPcs) CuPc and FePc, we discuss the temporal evolution of optically excited spin and charge carriers in these MPc /WSe₂ heterostructures. We will illustrate the influence of the distinct orbital character of the central metal atom and structural order of the MPc molecules on the ultrafast electron and hole dynamics at the MPc/WSe₂ interface and discuss their impact on the transient changes in the interfacial energy level alignment.

CPP 39.7 Thu 12:30 MA 004

Disentangling the multiorbital contributions of excitons by photoemission exciton tomography — ●G. S. MATTHIJS JANSSEN¹, WIEBKE BENNECKE¹, ANDREAS WINDISCHBACHER², RALF HEMM³, DAVID SCHMITT¹, JAN PHILIPP BANGE¹, CHRISTIAN KERN², DANIEL STEIL¹, SABINE STEIL¹, MARCEL REUTZEL¹, MARTIN

AESCHLIMANN³, PETER PUSCHNIG², BENJAMIN STADTMÜLLER^{3,4}, and STEFAN MATHIAS¹ — ¹I. Physikalisches Institut, Georg-August-Universität Göttingen — ²Institute of Physics, University of Graz — ³Department of Physics and Research Center OPTIMAS, University of Kaiserslautern — ⁴Institute of Physics, Johannes Gutenberg-University Mainz

The opto-electronic response of organic semiconductors is well-known to be dominated by excitons, i.e. quasiparticles that consist of bound electron-hole pairs. As excitons are realizations of a correlated many-particle wave function, experimental and theoretical methods must probe and characterize the the full electron-hole wavefunction, rather than just the single-particle orbitals. Recently, we have shown that time-resolved photoemission momentum microscopy can probe the entangled wavefunction and thereby unravel the exciton's multiorbital electron and hole contributions [1]. We demonstrate this for the prototypical organic semiconductor buckminsterfullerene (C₆₀) and achieve unprecedented access to key properties of the exciton state including localization, charge-transfer character, and ultrafast exciton formation and relaxation dynamics.

[1] W. Bennecke et al., arXiv preprint arXiv:2303.13904 (2023)

CPP 39.8 Thu 12:45 MA 004

Formation of charge-transfer excitons across the hybrid PTCDA/WSe₂ interface — ●WIEBKE BENNECKE¹, DAVID SCHMITT¹, JAN PHILIPP BANGE¹, IGNACIO GONZALEZ OLIVA², ANNA SEILER¹, LUKAS RENN¹, MATTIS LANGENDORF¹, DANIEL STEIL¹, SABINE STEIL¹, R. THOMAS WEITZ¹, PETER PUSCHNIG³, CLAUDIA DRAXL², MARCEL REUTZEL¹, G. S. MATTHIJS JANSSEN¹, and STEFAN MATHIAS¹ — ¹I. Physikalisches Institut, Georg-August-Universität Göttingen — ²Institut für Physik, Humboldt-Universität zu Berlin — ³Institute of Physics, University of Graz

Heterostructures consisting of van-der-Waals materials and organic molecules are a promising material platform due to their potential to combine the flexibility of organic chemistry with the remarkable opto-electronic properties of 2D materials. Here, we use femtosecond photoemission momentum microscopy to study ultrafast exciton dynamics in monolayer PTCDA adsorbed on WSe₂. By employing the concepts of photoemission orbital tomography, which has recently been shown to be capable of capturing key excitonic properties [1, 2], we are able to unambiguously identify the different excitonic states formed after optical excitation of WSe₂. We find that a localized long-lived charge-transfer exciton is formed on a picosecond timescale, where the hole resides in the WSe₂ and the electron is being transferred to the lowest unoccupied molecular orbital of PTCDA.

[1] C. Kern et al., *Phys. Rev. B* **108**, 085132 (2023)

[2] W. Bennecke et al., arXiv preprint arXiv:2303.13904 (2023)